

MONITORING OF POTENTIAL OCCUPATIONAL EXPOSURE
OF MIXER/LOADERS, PILOTS, AND FLAGGERS
DURING APPLICATION OF PHOSDRIN (MEVINPHOS)
IN IMPERIAL COUNTY IN 1981

by

Keith T. Maddy, Staff Toxicologist
Carl Winter, Environmental Hazards Specialist
Stacy Cepello, Environmental Hazards Specialist
A. Scott Fredrickson, Agricultural Chemist II

HS-889 Rev. January 21, 1982

Worker Health and Safety Unit
Division of Pest Management, Environmental Protection,
and Worker Safety
California Department of Food and Agriculture
1220 N Street, Sacramento, California 95814

SUMMARY

Potential inhalation and dermal exposure of mixer/loaders, pilots, and flaggers to Phosdrin (mevinphos) during routine commercial aerial applications were measured in Imperial County during April 1981. One aerial pest control operator firm was monitored for a period of 4 days. Air samples from the breathing zone, cloth pad samples placed on the outside of the workers' clothing, and handwash samples were collected. In addition, blood cholinesterase levels were measured prior to and at the conclusion of the study. Monitoring intervals ranged from 0.97 to 2.18 hours. Using results generated from the sampling, estimates were made of each worker's potential total exposure during a 7-hour workday. It was estimated that the mixer/loader (using closed-system transfer equipment) was exposed to levels of Phosdrin ranging from 342 to 1,343 micrograms per day, with a median of 861; the pilot was exposed to levels ranging from 56 to 469 micrograms, with a median of 120. Two flaggers were monitored each day during the study; their estimated exposures ranged from 0 to 9,622 micrograms of Phosdrin per day, with a median of 64. At the conclusion of the study, whole blood cholinesterase levels ranged from 85 percent of pre-exposure levels for the mixer/loader to 97 percent for the pilot, with the flaggers' levels found to be 94 and 96 percent. Assuming cholinesterase decreases of 20 to 25 percent are necessary to produce minimal incipient toxicity (Rider, 1975), and noting that humans exposed to levels of 0.025 mg/kg/day for 30 days did not show an average decrease in red blood cell or plasma cholinesterase exceeding the minimal incipient toxicity level (Verberk, 1977), it appears that Phosdrin exposures of mixer/loaders, pilots, and flaggers observing California Department of Food and Agriculture safe use regulations can be kept at low-hazard levels. Prior to the required use of closed-system transfer equipment, mixer-loaders exposures were from 10 to 100 times the amounts found in this study.

INTRODUCTION

In 1980, in the State of California, 14,693 applications of Phosdrin (mevinphos) were made to more than 524,903 acres of various crops, using 306,066 pounds of active ingredient (California Department of Food and Agriculture, 1981).

Phosdrin is one of the most toxic organophosphate chemicals used in California agriculture. Symptoms of Phosdrin poisoning, in common with other anti-cholinesterase agents, include headache, nausea, dizziness, sweating, weakness, ataxia, miosis, and muscle twitching.

Durham and Wolfe (1962) and Wolfe (1967) made measurements of air concentration levels for inhalation exposure and the levels of concentration on cloth patches at various body sites for dermal exposure, and calculated the total amount of various organophosphate pesticides that an individual worker might be exposed to; these studies did not include Phosdrin. It was proposed to study the inhalation and dermal exposure potential of mixer/loaders, pilots, and flaggers during aerial applications of Phosdrin during April 1981 in Imperial County.

MATERIALS AND METHODS

The cooperating aerial application firm selected for this study is located in Imperial County, and is a major pesticide applicator. This firm has an excellent record of compliance with established safe use regulations and work practices. All mixing, loading, and application procedures were performed in compliance with the Department's pesticide regulations, including using licensed pilots, providing clean coveralls daily, providing medical supervision with blood testing for cholinesterase levels, and using mechanical closed systems for mixing and loading.

Fixed-wing airplanes were used exclusively in this study. Reloading took place every 30 to 40 minutes.

The closed system that was utilized contained a manually operated probe which was placed into the proper opening of the pesticide container. A pump was used to draw the pesticide out of the container into the mix tank. Spray adjuvants and other pesticides were added to the mix tank when necessary. Contents of the mix tank were diluted with water to the desired concentration, using an inlet valve, and were pumped into the airplane. The exit end of the loading hose was equipped with an automatic shut-off coupler to prevent spillage.

The mixer/loader in this study wore shirts and pants under clean long-sleeve and long-leg cloth coveralls, heavy rubber gloves, and rubber boots. The pilot in this study wore long pants and long-sleeve shirts. Both flaggers wore overalls and long-sleeve shirts.

Monitoring periods were selected when at least 1 hour of continuous aerial application was expected to occur. Applications lasted from 1 to 2 hours.

No attempt was made to measure oral ingestion exposure. Potential inhalation exposure was measured by placing an MSA Model "S" portable air pump (at a flow rate of 1 cubic liter of air per minute) on each worker. The air intake hose was attached to the clothing under the chin area. Air sampling tubes containing Amberlite XAD-4 resin were inserted in the tygon air intake line.

Potential exposure to exposed skin area and skin protected by cotton coveralls was measured with patches made of an outer layer of 7-ounce 65 percent Dacron Polyester, 35 percent cotton twill, a middle layer of 100 percent cotton gauze, and an inner layer of aluminum foil. Each patch contained a premarked area of 49 cm² which could be cut out and analyzed. A single patch was placed on the back of the neck, on each upper arm, on each thigh, and on each side of the chest. Pre- and post-application handwash samples were taken by rinsing the workers' hands in approximately 250 ml of distilled water supplied by a separatory funnel.

Prior to any Phosdrin applications, in order to establish a baseline cholinesterase level, blood samples were drawn by licensed phlebotomists under contract with the State of California, and were shipped in iced containers by air freight to the Worker Safety laboratory in Sacramento. Two blood samples were taken at 24-hour intervals from all workers with the exception of the pilot, who gave only 1 sample. Each worker gave an additional blood sample immediately after conclusion of the final application. Cholinesterase activity in the blood samples was determined with a Techicon Autoanalyzer II system and the colorimetric method described by Knaak, et al (1978).

Upon conclusion of each application, the air sampling tubes and handwash samples were placed on ice in individual glass jars sealed with aluminum foil. The patches were removed from the clothing, the taped edges were cut off, and each gauze and outer cloth patch was carefully separated. Matched pairs of patches were placed together in glass jars (i.e., outside cloth of left and right arms combined, as were inside gauze and foil from left and right thighs). All samples were shipped in iced containers by air freight to Sacramento, and were received by the laboratory within 24 hours.

RESULTS

The results of the various experimental data and information are summarized in the following tables:

Table 1 - Air concentration levels monitored for inhalation exposure of various workers. Daily inhalation exposure (Column 3) was estimated by assuming an air inhalation volume of 1.74 m³/hour and 100 percent absorption by the lung (Spector, 1956).

Tables 2, 3, and 4 - The dermal exposure of workers determined by sampling patches. Column A is the sampling period. Column B is the results of Phosdrin exposure in micrograms per square centimeters. Column C is an estimate of the Phosdrin exposure in square centimeters adjusted for a typical full day (7 hours) exposure. Column D is an estimate of the

average area of the skin of each body part in square centimeters, according to Berkow (1931) and DuBois and DuBois (1916). This assumes an average person weighing 70 kg and standing 175 cm. Column E is an estimate of the dermal exposure to Phosdrin in micrograms per day to each body part. The calculations for the anterior portions of the head and neck use a combination of Phosdrin residues on the outside cloth and inside gauze samples placed on the chest to represent exposure of bare skin to airborne Phosdrin. Calculations for the posterior portion of the head and neck use a combination of the Phosdrin residues on the outside cloth and inside gauze sample placed on the back of the neck. Calculations for the anterior and posterior portions of the trunk use the gauze portions of the samples taken on the chest and back of the neck respectively. Similarly, the calculations for the arms and forearms use the gauze portion of the samples taken on the upper arms; the anterior legs and feet use the gauze portion of the samples taken on the thighs. Calculations for the posterior portion of the legs are derived by multiplying the back of neck/chest ratio by the thigh concentration. This is done after assuming that anterior and posterior exposures may differ, and that the back of neck-to-chest concentration ratio approximates the ratio of posterior-to-anterior leg concentration. Column F is the sum of the dermal exposure to the body parts, excluding the hands.

Table 5 - The dermal exposure of workers' hands using handwash sampling. Column A is the sampling period. Column B is the amount of Phosdrin found in the sample. Column C is the amount of Phosdrin estimated to be on the workers' hands at the end of a normal 7-hour workday.

Table 6 - Total of dermal and inhalation exposures during a full day's (7-hour) work with Phosdrin.

Appendix 1 - Use pattern data and information during aerial application of Phosdrin.

Table 7 - Pre- and post-application blood cholinesterase levels of workers.

Appendix 2 - Description of calculations used in Tables 2 to 5.

Appendix 3 - Description of Phosdrin extraction and analysis procedures.

DISCUSSION

Typical applications were monitored instead of setting up an "ideal" study with more control of variables. The cooperating firm was subject to California work practices and regulations that should have resulted in less exposure than would be typical in other states in the United States. For example, the required use of clean outer coveralls daily and the closed system for mixing and loading of Phosdrin would be expected to reduce daily inhalation and dermal exposure of workers as it has for other pesticides studied.

The inhalation exposure, in micrograms per cubic meter of air, was found to be at levels ranging from 5 to 11 for the mixer/loader, from 3 to 13 for the pilot, and from below the detectability limit of 0.2 to 55 for the flaggers. As all values are much below the established time-weighted average (TWA) of 100 micrograms per cubic meter (ACGIH, 1979), inhalation exposure to Phosdrin would not seem to present health hazards to the workers monitored.

In order to simulate whole body dermal exposure due to penetration through the coveralls, cloth pads were designed with 3 layers of material. The outer layer was coverall material; a second layer consisted of heavy cotton gauze; the final layer was aluminum foil. The amount that penetrated the top layer and became entrapped in the gauze was considered to be the amount that might penetrate the coveralls and reach the skin.

A legend explaining the method of calculations used in Tables 2 to 4 is found in Appendix 2. The most extreme dermal exposure situation occurs when no clothing is worn under a worker's coveralls; sometimes varying amounts of clothing are worn under the coveralls.

The major route of Phosdrin exposure appears to be dermal. The mixer/loader was exposed to amounts ranging from a low of 0 to a high of 600 micrograms (excluding hand exposure); the pilot was exposed to levels ranging from 0 to 215 micrograms. Flaggers were exposed to levels from 0 to 7,981 micrograms. Exposure of hands, measured by handwash samples, in micrograms per 7-hour workday, ranged from 134 to 1,190 for the mixer/loader, from 0 to 73 for the pilot, and from 0 to 875 for the flaggers.

Rider (1975) has defined "minimal incipient toxicity" as the concentration of a cholinesterase-inhibiting pesticide, when ingested daily over a period of 30 days, which will produce an average decrease in the plasma and/or red blood cell cholinesterase of 20 to 25 percent. Other articles (Gage, 1967; Biological Monitoring, 1976) suggest that action may have to be taken to minimize exposure to anti-cholinesterase agents if a 30 percent depression from the baseline for red blood cell or whole blood cholinesterase levels occurs. California regulations require that an employer remove an employee from all work exposure to organophosphates or carbamates if plasma cholinesterase and red blood cell cholinesterase levels decrease 50 and 40 percent respectively from the employee's pre-established baseline levels (California Department of Food and Agriculture, 1979).

The blood data obtained in this study indicate that cholinesterase depression in the workers was probably not large enough to produce any symptomatology. Maximum depression occurred in the mixer/loader, resulting in a total cholinesterase decrease of 15 percent from his baseline concentration. It should be noted that during the study all workers were also exposed to other cholinesterase-inhibiting pesticides which might have also led to cholinesterase decreases.

Rider (1975) and Verberk (1977) have performed studies to determine the no-observable effect level (NOEL) for human volunteers ingesting Phosdrin for 30 consecutive days. This level is defined as the amount of Phosdrin

necessary to produce plasma and/or red blood cell cholinesterase decreases of 20-25 percent when ingested orally. Verberk found a NOEL of 0.025 mg/kg/day Phosdrin while Rider's value was reported to be 0.014 mg/kg/day. Verberk's NOEL is accepted as a more accurate value because larger test and control groups were used.

Little information exists relating the dermal toxicity of Phosdrin to its oral toxicity. The oral LD₅₀ has been reported to be 3.7 mg/kg, and the dermal LD₅₀ has been reported to be 4.2 mg/kg (University of California, 1979). We will assume that the oral toxicity of Phosdrin exceeds its dermal toxicity on the basis of more rapid and complete absorption into the blood. Studies have shown that required California practices such as bathing daily and wearing clean coveralls lead to decreases in dermal absorption of related pesticides (Durham, et al, 1972). Therefore, if daily worker dermal exposure to Phosdrin is less than the oral NOEL, we would expect no symptomology or significant cholinesterase depression.

CONCLUSION

Phosdrin exposure of the mixer/loader, pilot, and flaggers in this study, measured by dermal and inhalation sampling and by blood cholinesterase testing, appears to be low enough to suggest that present California Department of Food and Agriculture safe use regulations are adequate in ensuring worker safety with this chemical. Median potential exposure of all workers was below the daily oral NOEL and none of the blood cholinesterase levels were shown to meet the criteria established for "minimal incipient toxicity."

As might have been expected, the mixer/loader showed the highest median exposure and greatest cholinesterase depression. This median exposure level, 0.861 milligrams per day, represents a daily dosage of 0.861 mg/70kg/day, or 0.012 mg/kg/day for the average 70-kg human, corresponding to 48 percent of the oral NOEL. Whole blood cholinesterase was decreased 15 percent, plasma levels decreased 19 percent, and red blood cell levels dropped 13 percent. All of these values are below the estimated 20 to 25 percent decrease necessary to indicate a toxic reaction. The low exposure of the mixer/loader is primarily the result of careful work practices and the careful use of closed mixing and loading systems that allow the use of highly toxic products without the need for bulky impervious protective clothing. Before application firms began using closed system equipment 6 years ago, severely depressed cholinesterase values and serious poisonings were common events; exposures of 10 to 100 times the amounts found in this study were not unusual.

The largest single daily exposure, 9.622 milligrams, was from Flagger II, day 4. It should be noted that no symptomology was observed following this exposure, and that cholinesterase levels taken after the exposure showed only slight depression from pre-exposure levels (see table 7).

REFERENCES

1. Rider, J. A., E. J. Puletti, and J. I. Swider: The Minimal Oral Toxicity Level for Mevinphos in Man. Toxicol. Appl. Pharmacol. 32:97-100 (1975).
2. Verberk, M. M.: Incipient Cholinesterase Inhibition in Volunteers Ingesting Monocrotophos or Mevinphos for One Month. Toxicol. Appl. Pharmacol. 42:345-350 (1977).
3. California Department of Food and Agriculture: Pesticide Use Report Annual 1980, p. 154-155, Sacramento, CA (1981).
4. Durham, W. F., and H. R. Wolfe: Measurement of Exposure of Workers to Pesticides. Bull. WHO 26:75-91 (1962).
5. Wolfe, H. R., and W. F. Durham: Exposure of Workers to Pesticides. Arch. Environ. Health 14:622-633 (1967).
6. Knaak, J. B., K. T. Maddy, T. Jackson, A. S. Fredrickson, S. A. Peoples, and R. Love: Cholinesterase Activity in Blood Samples Collected From Field Workers and Nonfield Workers in California. Toxicol. Appl. Pharmacol. 45:755 (1978).
7. Spector, W. S.: Handbook of Biological Data. Saunders, Philadelphia, PA (1956).
8. Berkow, S. G.: Value of Surface Area Proportions in the Prognosis of Cutaneous Burns and Scalds. Am. J. Surg. 11:315-317 (1931).
9. DuBois, D., and E. E. DuBois: A Formula to Estimate the Approximate Surface Area if Height and Weight Be Known. Arch. Int. Med. 17:863 (1916).
10. American Conference of Government Industrial Hygienists: Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1979. Cincinnati, OH (1979).
11. Gage, J. C.: The Significance of Blood Cholinesterase Activity Measurements. Residue Reviews 18:159-173 (1967).
12. Biological Monitoring in Exposure to Cholinesterase Inhibitors. Int. Arch. Occup. Environ. Health 37:65-71 (1976).
13. California Department of Food and Agriculture, Worker Health and Safety Unit: Extracts from the California Administrative Code. HS-036, Sacramento, CA (1979).
14. University of California, Division of Agricultural Sciences: Pesticide Toxicities p. 19, Leaflet 21062 (1979).

15. Durham, W. F., H. R. Wolfe, and J. W. Elliot: Absorption and Excretion of Parathion by Spraymen. Arch. Environ. Health 24:381-387 (1972).
16. Jackson, T.: Analysis of XAD-4 Resin. CDFA Worker Safety Method, Sacramento, CA (February 5, 1976).

Table 1

Amount of Phosdrin Found in the Breathing Zone
of Mixer/Loader, Pilot, and Flaggers

Worker	Day	Column 1	Column 2	Column 3
		ppb (V.V)	Mg/m ³	Estimated Daily Inhalation Exposure for 7-Hour Day (Micrograms)
Mixer/Loader	1	0.56	0.005	70
Mixer/Loader	2	1.21	0.011	153
Mixer/Loader	3	0.16	0.002	28
Mixer/Loader	4	0.74	0.007	97
Pilot	1	0.70	0.006	84
Pilot	2	1.38	0.013	181
Pilot	3	0.32	0.003	42
Pilot	4	0.74	0.007	97
Flagger I	1	ND	ND	0
Flagger I	2	ND	ND	0
Flagger I	3	0.049	0.0004	6
Flagger I	4	1.51	0.014	195
Flagger II	1	ND	ND	0
Flagger II	2	1.16	0.011	153
Flagger II	3	0.16	0.002	28
Flagger II	4	5.98	0.055	766

Dermal Phosdrin Exposure
to Mixer/Loader (Excluding Hands)

Total

Table 2 (Cont.)

Dermal Phosdrin Exposure
to Mixer/Loader (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F					
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Area of Skin Surface (cm ²)	Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)	
			Outside Cloth	Inside Gauze			Covered Skin	Bare Skin		Covered Skin
Mixer/Loader, Day 3	Face, head and neck, anterior	2.03	ND	ND	ND	-	810	-	0	-
	Head and neck, posterior	2.03	ND	ND	ND	-	300	-	0	-
	Trunk, anterior	2.03	ND	ND	ND	3,700	-	0	-	-
	Trunk, posterior	2.03	ND	ND	ND	3,300	-	0	-	-
	Arms and forearms	2.03	ND	ND	ND	2,498	-	0	-	-
	Legs and feet, anterior	2.03	0.005	ND	ND	3,515	-	0	-	-
	Legs, posterior	2.03	ND	ND	ND	3,515	-	0	-	-
Total										0

Table 2 (Cont.)

Dermal Phosdrin Exposure

Worker	Skin Area Studied	Column A		Column B		Column C		Column D				Column E		Column F	
		Hours of Exposure		Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)		Area of Skin Surface (cm ²)		Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)			
		Hours of Exposure	Skin Area Studied	Outside Cloth	Inside Gauze	Outside Cloth	Inside Gauze	Covered Skin	Bare Skin	Covered Skin	Bare Skin	Covered Skin	Bare Skin		
Mixer/Loader, Day 4	Face, head and neck, anterior	1.77		0.161	ND	0.638	ND	-	810	-	517	-	-	-	-
	Head and neck, posterior	1.77		0.070	ND	0.277	ND	-	300	-	83	-	-	-	-
	Trunk, anterior	1.77		0.161	ND	0.638	ND	3,700	-	0	-	0	-	-	-
	Trunk, posterior	1.77		0.070	ND	0.277	ND	3,300	-	0	-	0	-	-	-
	Arms and forearms	1.77		0.014	ND	0.055	ND	2,498	-	0	-	0	-	-	-
	Legs and feet, anterior	1.77		0.011	ND	0.044	ND	3,515	-	0	-	0	-	-	-
	Legs, posterior	1.77		0.005	ND	0.020	ND	3,515	-	0	-	0	-	-	-

Total

609

Table 3

Dermal Phosdrin Exposure
to Pilot (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F	
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
			Outside Cloth	Inside Gauze		
Covered Skin	Bare Skin	Covered Skin	Bare Skin	Covered Skin	Bare Skin	
						Area of Skin Surface (cm ²)
Covered Skin	Bare Skin	Covered Skin	Bare Skin	Covered Skin	Bare Skin	
						3,700
3,300	300	0	0	0	0	
						2,498
3,515	0	0	0	0	0	
						3,515
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0
0	0	0	0	0	0	
						0

Table 3 (Cont.)

215

Table 3 (Cont.)

Dermal Phosdrin Exposure
to Pilot (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F						
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Area of Skin Surface (cm ²)		Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)	
			Outside Cloth	Inside Gauze		Covered Skin	Bare Skin	Covered Skin	Bare Skin		
Pilot, Day 3	Face, head and neck, anterior	2.03	0.005	ND	0.017	ND	-	810	-	14	-
	Head and neck, posterior	2.03	ND	ND	ND	ND	-	300	-	0	-
	Trunk, anterior	2.03	0.005	ND	0.017	ND	3,700	-	0	-	-
	Trunk, posterior	2.03	ND	ND	ND	ND	3,300	-	0	-	-
	Arms and forearms	2.03	ND	ND	ND	ND	2,498	-	0	-	-
	Legs and feet, anterior	2.03	ND	ND	ND	ND	3,515	-	0	-	-
	Legs, posterior	2.03	ND	ND	ND	ND	3,515	-	0	-	-

Table 3 (Cont.)

Dermal Phosdrin Exposure
to Pilot (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F						
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)		Area of Skin Surface (cm ²)		Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
			Outside Cloth	Inside Gauze	Outside Cloth	Inside Gauze	Covered Skin	Bare Skin	Covered Skin	Bare Skin	
Pilot, Day 4	Face, head and neck, anterior	2.10	0.005	ND	0.017	ND	-	810	-	14	-
	Head and neck, posterior	2.10	0.013	ND	0.043	ND	-	300	-	13	-
	Trunk, anterior	2.10	0.005	ND	0.017	ND	3,700	-	0	-	-
	Trunk, posterior	2.10	0.013	ND	0.043	ND	3,300	-	0	-	-
	Arms and forearms	2.10	0.034	ND	0.113	ND	2,498	-	0	-	-
	Legs and feet, anterior	2.10	0.031	ND	0.103	ND	3,515	-	0	-	-
	Legs, posterior	2.10	0.081	ND	0.270	ND	3,515	-	0	-	-

Total

27

Table 4

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)

[illegible]

Table 4 (Cont.)

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F							
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Dermal Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Area of Skin Surface (cm ²)	Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)			
			Outside Cloth	Inside Gauze			Outside Cloth	Inside Gauze		Covered Skin	Bare Skin	
Flagger 1, Day 2	Face, head and neck, anterior	1.75	ND	ND	ND	ND	-	810	-	0	-	
	Head and neck, posterior	1.75	ND	ND	ND	ND	ND	-	300	-	0	-
	Trunk, anterior	1.75	ND	ND	ND	ND	ND	3,700	-	0	-	-
	Trunk, posterior	1.75	ND	ND	ND	ND	ND	3,300	-	0	-	-
	Arms and forearms	1.75	ND	ND	ND	ND	ND	2,498	-	0	-	-
	Legs and feet, anterior	1.75	ND	ND	ND	ND	ND	3,515	-	0	-	-
	Legs, posterior	1.75	ND	ND	ND	ND	ND	3,515	-	0	-	-
Total												0

Table 4 (Cont.)

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)

Column A		Column B				Column C				Column D				Column E				Column F	
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)		Area of Skin Surface (cm ²)		Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)								
			Outside Cloth	Inside Gauze	Outside Cloth	Inside Gauze	Covered Skin	Bare Skin	Covered Skin	Bare Skin	Covered Skin	Bare Skin							
Flagger 1, Day 3	Face, head and neck, anterior	2.18	0.018	ND	ND	0.058	ND	-	810	-	47	-	-						
	Head and neck, posterior	2.18	ND	ND	ND	ND	ND	-	300	-	0	-	-						
	Trunk, anterior	2.18	0.018	ND	ND	0.058	ND	3,700	-	0	-	-	-						
	Trunk, posterior	2.18	ND	ND	ND	ND	ND	3,300	-	0	-	-	-						
	Arms and forearms	2.18	0.020	ND	ND	0.064	ND	2,498	-	0	-	-	-						
	Legs and feet, anterior	2.18	0.021	ND	ND	0.067	ND	3,515	-	0	-	-	-						
	Legs, posterior	2.18	ND	ND	ND	ND	ND	3,515	-	0	-	-	-						

Total

47

Table 4 (Cont.)

Total

1,136

Table 4 (Cont.)

•

Table 4 (Cont.)

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F						
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)		Area of Skin Surface (cm ²)		Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
			Outside Cloth	Inside Gauze	Outside Cloth	Inside Gauze	Covered Skin	Bare Skin	Covered Skin	Bare Skin	
Flagger II, Day 2	Face, head and neck, anterior	1.75	ND	ND	ND	ND	-	810	-	0	-
	Head and neck, posterior	1.75	ND	ND	ND	ND	-	300	-	0	-
	Trunk, anterior	1.75	ND	ND	ND	ND	3,700	-	0	-	-
	Trunk, posterior	1.75	ND	ND	ND	ND	3,300	-	0	-	-
	Arms and forearms	1.75	0.014	ND	0.056	ND	2,498	-	0	-	-
	Legs and feet, anterior	1.75	0.014	ND	0.056	ND	3,515	-	0	-	-
	Legs, posterior	1.75	ND	ND	ND	ND	3,515	-	0	-	-
Total											0

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)[illegible]

Table 4 (Cont.)

Dermal Phosdrin Exposure
to Flaggers (Excluding Hands)

Column A	Column B	Column C	Column D	Column E	Column F						
Worker	Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads (mg/cm ²)		Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Area of Skin Surface (cm ²)	Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)		Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)		
			Outside Cloth	Inside Gauze			Covered Skin	Bare Skin		Covered Skin	Bare Skin
Flagger II, Day 4	Face, head and neck, anterior	2.00	0.201	0.149	0.704	0.522	-	810	-	993	-
	Head and neck, posterior	2.00	0.020	*0.015	0.070	0.053	-	300	-	37	-
	Trunk, anterior	2.00	0.201	0.149	0.704	0.522	3,700	-	1,931	-	-
	Trunk, posterior	2.00	0.020	*0.015	0.070	0.053	3,300	-	176	-	-
	Arms and forearms	2.00	0.449	0.316	1.572	1.106	2,498	-	2,763	-	-
	Legs and feet, anterior	2.00	0.205	0.154	0.718	0.539	3,515	-	1,895	-	-
	Legs, posterior	2.00	0.020	*0.015	0.070	0.053	3,515	-	186	-	-

* Estimated Value

Table 5

Amount of Phosdrin Found on Hands
of Mixer/Loader, Pilot, and Flaggers

Worker	Day	Column A	Column B	Column C
		Hours of Exposure	Results in Micrograms per Sample	Micrograms Adjusted to 7-Hours of Exposure
Mixer/Loader	1	1.25	24	134
Mixer/Loader	2	1.73	294	1,190
Mixer/Loader	3	2.03	91	314
Mixer/Loader	4	1.77	163	645
Pilot	1	1.08	ND	0
Pilot	2	1.82	19	73
Pilot	3	2.03	ND	0
Pilot	4	2.10	10	33
Flagger I	1	1.07	ND	0
Flagger I	2	1.75	ND	0
Flagger I	3	2.18	15	48
Flagger I	4	2.00	36	126
Flagger II	1	0.97	ND	0
Flagger II	2	1.75	5	20
Flagger II	3	2.13	ND	0
Flagger II	4	2.00	250	875

Table 6

Total Estimated Dermal and Inhalation
Exposure for 7-Hour Work Period

Worker	Day	Estimated Phosdrin Dermal Exposure for Average 7-Hour Exposure (Excluding hands) (Micrograms)	Estimated Phosdrin Dermal Exposure to the the Hands for Average 7-Hour Exposure (Micrograms)	Estimated Phosdrin Inhalation Exposure for Average 7-Hour Work period (Micrograms)	Total Estimated Phosdrin Exposure During 7-Hour Work period (Micrograms)
Mixer/Loader	1	176	134	70	380
Mixer/Loader	2	0	1,190	153	1,343
Mixer/Loader	3	0	314	28	342
Mixer/Loader	4	600	645	97	1,342
Pilot	1	0	0	84	84
Pilot	2	215	73	181	469
Pilot	3	14	0	42	56
Pilot	4	27	33	97	157
Flagger I	1	0	0	0	0
Flagger I	2	0	0	0	0
Flagger I	3	47	48	6	101
Flagger I	4	1,136	126	195	1,457
Flagger II	1	0	0	0	0
Flagger II	2	0	20	153	173
Flagger II	3	0	0	28	28
Flagger II	4	7,981	875	766	9,622

Table 7

Workers' Pre- and Post-Application
Cholinesterase Levels
(Micromoles - SH/ml/min)

WORKER	Pre-Application						Post-Application								
	Sample #1			Sample #2			Average			% of Aver. Pre-App.					
	Whole Blood	Plasma	RBC	Whole Blood	Plasma	RBC	Whole Blood	Plasma	RBC	Whole Blood	Plasma	RBC			
MIXER/LOADER	13.6	6.8	22.0	13.4	7.2	21.0	13.5	7.0	21.5	11.5	5.7	18.8	85	81	87
PILOT	17.0	8.2	27.6	-	-	-	17.0	8.2	27.6	16.5	7.9	26.9	97	96	97
FLAGGER I	16.7	6.3	28.5	18.0	6.7	31.3	17.4	6.5	29.9	16.7	6.7	28.0	96	103	94
FLAGGER II	18.5	8.5	31.2	19.0	9.6	30.5	18.8	9.0	30.8	17.8	8.4	28.4	95	93	92

Table 2 (Cont.)

**Dermal Phosdrin Exposure
to Mixer/Loader (Excluding Hands)**

Column A	Column B	Column C	Column D	Column E	Column F
Skin Area Studied	Hours of Exposure	Amount of Phosdrin on Cloth Pads ₂ (mg/cm ²)	Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²)	Area of Skin Surface (cm ²)	Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands)
		Outside Cloth	Inside Gauze	Covered Skin	Bare Skin
Mixer/ Loader, Day 2	1.73	ND	ND	-	810
Head and neck, posterior	1.73	ND	ND	-	300
Trunk, anterior	1.73	NS	ND	3,700	-
Trunk, posterior	1.73	ND	ND	3,300	-
Arms and forearms	1.73	ND	ND	2,498	-
Legs and feet, anterior	1.73	0.013	ND	3,515	-
Legs, posterior	1.73	ND	ND	3,515	-
Total					0

APPENDIX 1
APPLICATION INFORMATION

	<u>Day 1</u>	<u>Day 2</u>	<u>Day 3</u>	<u>Day 4</u>
Pesticide Used	Durham Duraphos 400	Durham Duraphos 400	Durham Duraphos 400	Durham Duraphos 400
EPA Reg. No.	05481-00114AA	05481-00114AA	05481-00114AA	05481-00114AA
Carrier Used	Water	Water	Water	Water
Dilution Used	1 pint/ 5 gal. H ₂ O	0.85 pints/ 5 gal. H ₂ O	1 pint/ 5 gal. H ₂ O	1 pint/ 5 gal. H ₂ O
Other Chemicals Used	None	Malathion 8, Manzate	None	None
Application Time (hours)	1.25	1.82	2.18	2.10
Beginning Temp. (°C)	26	36	24	38
Ending Temp. (°C)	28	30	22	34

APPENDIX 2 - Explanation of
Calculations Used for the
Various Columns of Tables 2 to 4

Below are the methods of calculations used for Tables 2-4:

COLUMN B: Amount of Phosdrin found by analysis in sample.

COLUMN C: $\frac{7 \times (\text{Column B})}{\text{Column A}}$

COLUMN D: From Berkow (1931) and DuBois and DuBois (1916).

COLUMN E: (Column C) X (Column D).

COLUMN F: Sum of values from Column E.

Appendix 3

Phosdrin Extraction and Analysis Procedures

Extraction of Phosdrin from Cloth Patches

25 ml of acetone was added to the patches (approximately 49 cm²). The sample containers were sealed with aluminum foil and rotated 15 minutes on a jar roller at 30 rpm. Gauze was treated in a similar manner. A portion of the extract was analyzed by gas chromatography without further treatment.

GLC Conditions:

Instrument: Hewlett Packard 5880 with NPD detector at 250°C.

Column: 6 ft. x 2 mm glass packed with 10 percent SP-2100 coated on Chromosorb W-HP operating at 160°C. and 35 ml/min helium carrier gas.

Injector: On column injection, 220°C.

Under these conditions, Phosdrin eluted in 3.25 minutes. There were no interfering materials, and recovery was greater than 95 percent.

Phosdrin in Water Handwashes

Reagents and Equipment:

1. Ethyl acetate, nanograde.
2. Sodium sulfate.
3. 500 ml graduated cylinder.
4. Assorted volumetric glassware and pipets as needed for samples and standards.
5. Gas chromatography:

Instrument: Hewlett Packard 5880 with NPD detector.

Column: 6 ft. x 2 mm glass column containing 10 percent SP-2100 coated on 100/120 mesh Chromosorb W-HP operating at 160°C. and 35 ml/min helium carrier gas.

Temperatures: Detector at 300°C.
Injector at 220°C.

Under these conditions, Phosdrin eluted in about 3.25 minutes.

Analysis:

The amount of solution was measured and recorded. A 100 ml aliquot was placed in a 250 ml separatory funnel. Ten ml saturated NaCl solution was added, and 50 ml ethyl acetate was added for extraction. The water layer was drained, and the ethyl acetate layer was placed in a 100 ml glass-stoppered graduate. The water layer was then reextracted twice with 20 ml ethyl acetate. The extracts were combined in the graduate. The extracts were brought to volume, and sufficient sodium sulfate was added to dry the solvent. Analysis was by GLC.

Recoveries were in excess of 95 percent.

Phosdrin on XAD-4 Air Sample Tubes

Reagents and Equipment:

1. Acetone, nanograde.
2. Analytical grade Phosdrin.
3. Approved and calibrated personal sampling pump.
4. XAD-4 resin tubes, SKC or equivalent.
5. Developing vials with teflon septum caps, SKC #226-02 or equivalent.
6. Tube breaking kit, triangular file, tweezers, paper clip, etc.
7. Assorted volumetric glassware and pipets as needed for standards and samples.
8. Hewlett Packard 5880 gas chromatograph with NPD detector.
9. 6 ft. x 2 mm 10 percent SP-2100 on Chromosorb WHP 100/120 mesh glass column.
10. Starting GC parameters with the above column were:
 - a. Injector = 260°C.
 - b. Column = 160°C. and 35 ml/min helium carrier gas.
 - c. Detector = 300°C.

Analysis:

Interferences: High humidity may affect trapping efficiency.

1. Each sample tube was scored with a file in front of the first section of the resin.

2. Tubes were then broken open.
3. The wire was removed and disposed of.
4. The glass wool, the first (larger) section of resin, and the central foam plug were transferred into a desorption vial containing 3 ml of acetone, and labeled as "front section".
5. The backup portion of the resin was transferred into another desorption vial containing 3 ml of acetone, and labeled as back portion.
6. The desorption vials were then placed on a sample rotator and rotated for 1 hour.
7. The amount of Phosdrin present was determined by gas chromatography.

Determination of Desorption Efficiency:

1. The foam and second (small) portion of resin was removed from an XAD-4 tube of the same lot number to be used for the determinations.
2. A known and reasonable amount (calculated from the amount required to add from the anticipated level of Phosdrin expected in the field or the desired sensitivity) of Phosdrin standard was injected into the remaining section of resin in the tube with a microsyringe. The tube was capped and stored as it would have been during sample shipment. The storage time should be the same as the time expected to elapse between taking the sample and analyzing it.
3. The mean value was determined by running 5 tubes in this manner.
4. Desorption efficiency = $(\text{Area sample} - \text{Area blank}) / (\text{Area standard})$ where the standard is the same amount as injected into the tube.
5. A check on the absorption coefficient was made by following steps 1 and 2 and placing the spiked sample tube on an air pump and drawing a representative volume of air through the tube at a representative sampling rate before storage. This determination is much easier when leaving the back portion of resin in the tube.

Calculations:

1. The weight of Phosdrin present on tube section was determined by gas chromatographic analysis in nanograms.
2. Total weight was corrected by subtracting any weight value from the blank or control tube.
3. The corrected weight was divided by the determined desorption efficiency (and adsorption efficiency if needed) to obtain the final corrected weight of Phosdrin present.

4. The volume of air sampled was converted to stand conditions of 25°C. and 760 mm Hg.

$$VS = (V \times P \times 298) / (760 \times [T + 273])$$

where:

VS = volume of air at STP
V = volume of air as measured
P = barometric pressure in mm Hg
T = temperature of the air in degrees Centigrade.

5. Ppb vapor phase in the air was calculated from the above data.

$$\text{ppb v/v} = (ns \times 24.45) / (VS \times 224)$$

where:

ns = corrected nanograms (#3)
VS = corrected air volume in liters (#4)
224 = molecular weight of Phosdrin.

for Phosdrin at 25°C.,

$$\text{ppb v/v} = (ns \times 0.10915) / VS.$$